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MODIFICATION OF QUARTZ – LIQUID GLASS COMPOSITES WITH ORGANIC RESINS

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The effect of organic resins on the strength characteristics and pore structure of quartz – liquid glass composites was investigated. It was found that use of liquid glass modified with 5% PAN-19 polyester resin as the binder allows increasing the strength by 25 – 30% and decreasing water absorption by 40%. The total porosity of the modified composition decreased by 30% in comparison to the composition with no additives and the average pore size also decreased and pores 0 – 0.2 mm in size totally disappeared.

Liquid-glass compositions with complex quartz or another acid-resistant filler are binder systems which can be used to obtain materials with a wide spectrum of technological properties by altering the composition and processing parameters. They can be used as a binder for general- and special-purpose construction materials, heat insulating, fireproofing, and chemically stable articles.

The compositions based on liquid glass and a quartz filler of defined granulometric composition have a series of such unique properties as corrosion resistance, heat resistance, high adhesion to metals, and the ability to precisely re-create the impression of a shape. The use of pigments and corresponding technologies for preparation of molding pastes allows obtaining man-made stone that simulates natural granite, marble, malachite, serpentine, turquoise, etc. In this way, it becomes possible to use the composition for fabricating paving blocks, facing and floor tiles, designer elements for fireplaces, fountains, staircases, foundations, outer walls, in landscape design, and in restoration of architectural monuments.

However, materials containing liquid glass as a binder have many important drawbacks: high water absorption and porosity, low strength. This is due to the presence of a large amount of silicic acid gel, which has a highly developed surface and microporosity, in the hardened stone (Fig. 1).

Partial replacement of the usual filler (quartz sand) with active powdered quartz combined with modification of the binder with polymeric resins allowed significantly increasing the structural and technical characteristics of the material. Silicate materials modified with organic additives that are both polymer dispersions and synthetic resins to increase the strength and corrosion resistance are now being actively developed. There is a large number of organic modifiers of liquid glass. Epoxy resins and compounds containing ester bonds are most frequently used for this purpose, and their presence causes the appearance of carboxyl groups in the reaction mass. The products of polymerization of organic resins are adsorbed on the surface of filler particles, forming an elastic layer, and they also partially clog the pores and make the surface of their walls hydrophobic [1]. For this reason, it would be very interesting to study the effect of polyester and epoxy resins on the microstructure and process characteristics of materials based on liquid glass.

The studies were conducted on standard samples measuring $1 \times 1 \times 33$ cm prepared with casting technology and hardened in natural conditions for 28 days. Standard samples measuring $4 \times 4 \times 16$ cm were used to determine the water

Fig. 1. Microstructure of stone ($\times$ 1000).

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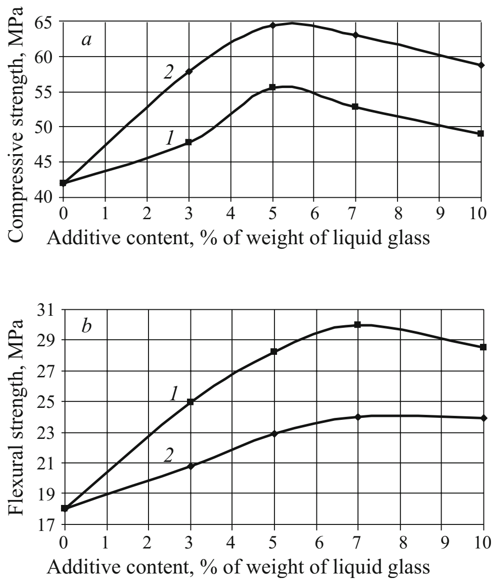

Fig. 2. Compressive strength (*a*) and flexural strength (*b*) as a function of the ÉPD-20 (*1*) and PN-19 (*2*) content.

resistance coefficient. We investigated compositions containing ordinary and ground (specific surface area of 5000 cm^2/g) quartz sand in the ratio of 1 : 1, 22.3%[2] sodium liquid glass (modulus 3.0, density 1.38 g/cm^3) and 3.3% sodium silicofluoride, Na_2SiF_6. The liquid glass was modified with ÉPD-20 epoxy resin and PN-19 polyester resin. The additive content was 3, 5, 7, and 10% of the weight of the liquid glass.

The compressive and flexural strength, water absorption, and water resistance coefficient were determined on the samples. The pore structure of the samples of basic composition and the composition containing the optimum amount of modifier additive with respect to the strength was evaluated by optical microscopy.

The curves of the strength characteristics as a function of the type and amount of additive are shown in Fig. 2.

The reaction of organic and inorganic components in the structure of the material basically consists of adsorption of the polymer on the walls of pores and grains of filler, but it is not possible to exclude partial copolymerization of silica and organic resins in the contact zone. Films of products of polymerization of the organic resin form on the highly developed surface of the silicic acid xerogel, and this increases the elasticity of the entire system. The presence of a large number of such polymer films, which adhere well to mineral components, in the microstructure of the material also increases the resistance to destructive effects. It is necessary to note that the curves shown in Fig. 2 are extremal in character. Addition of polyester resin in the amount of 5% of the weight of the binder allows obtaining the maximum compressive strength — of the order of 60 MPa, and when liquid glass modified with 7% epoxy resin is used, the flexural strength increases from 18 (basic composition) to 30 MPa. This selective effect on the properties is probably due to a difference in the mechanical characteristics of the polymer films themselves and the strength of the adhesive contacts between the mineral and organic components.

[2] Here and below: mass content.

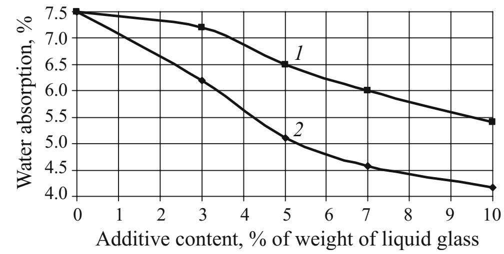

Fig. 3. Water absorption as a function of ÉPD-20 (*1*) and PN-19 (*2*) content.

The water absorption of construction materials is of great interest, since it characterizes the open porosity, which in turn is directly correlated with cold resistance, where low values limit the area of application of liquid-glass compositions. The results of studying the effect of polymer resin additives on water absorption are shown in Fig. 3.

The water absorption monotonically decreases with an increase in the resin content in the investigated composition range. Polyester resin is more effective than epoxy resin — incorporation of 10% PN-19 decreases water absorption from 7.5 to 4.2%. This effect is probably due to an important change in the microstructure of the stone. The effect of modifiers is manifested in the initial stages of hardening. The products of polymerization of the organic resin are adsorbed on the $Si(OH)_4$ gel nuclei formed in the hardening system. The appearance of such films on the surface of associates blocks their further enlargement and thus causes the formation of a larger number of gel phase nuclei and consequently formation of a more regular and dense structure [1].

It is believed that ordinary compositions based on bulk-hardened liquid glass are not distinguished by good water resistance. We tested the samples for water resistance, since this characteristic is very important in determining the directions for use of the material in humid conditions. The water resistance was assessed with the water resistance coefficient, determined as the ratio of the flexural strength of samples held in aqueous medium for 360 days to the strength of the samples before they were immersed in the water.

Effect of the Additive Type and Content on the Water Resistance of the Material

Additive content, % of weight of liquid glass	Water resistance coefficient
0	1.79
PN-19:	
5	1.22
10	0.98
ÉDP-20:	
5	1.05
10	0.89

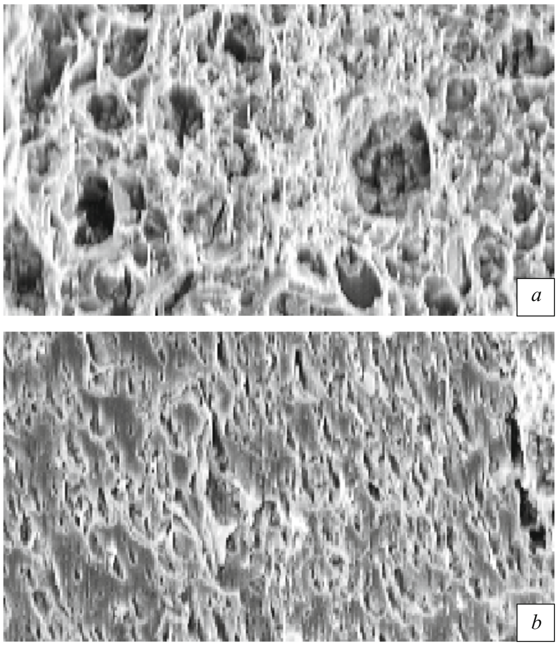

Fig. 4. Microstructure (× 450) of sample of base composition (*a*) and sample modified with 5% PN-19 resin (*b*).

TABLE 1

Parameter	Composition: base	Composition: with 5% PN-19 resin
Porosity, %	9.03	6.36
Total area analyzed, mm^2	20.54	20.54
Number of pores per unit of volume, mm^{-1}	1662.51	1414.55
Average thickness of walls between pores, mm	0.12	0.17
Number of pores in plane of section	1207	942
Pore size, mm:		
total perimeter	116.8	76.9
total area	1.85	1.31
average area	0.02	0.01
average perimeter	0.10	0.08
average diameter	0.03	0.03
Average pore shape factor	0.60	0.68
Pore diameter, mm:		
maximum	0.36	0.29
minimum	0.01	0.01

It was found that increasing the dispersion of the quartz filler particles allows significantly increasing the water resistance coefficient, and with fineness of grinding the quartz to a specific surface area of the order of 5000 cm^2/g, the flexural strength even increased, by 80%, in storage in water for one year.

The use of organic polymer resins for modification of liquid glass decreases the water resistance of the stone in comparison to the additive-free composition. The greatest decrease is observed for epoxy resin. This is probably due to the reduced water resistance of the polymer. The indexes for polyester resin are better, as degradation of the polymer is much less due to the effect of the aqueous medium. However, we must emphasize that judging by the results of the tests, all samples were absolutely water resistant, since their water resistance coefficient was over 0.8 even when epoxy resin, which is not water resistance per se, was added.

An optical microscopic analysis of a sample with 5% PN-19 (optimum amount) and a sample of base composition (× 100) was conducted for a more detailed explanation of the effect of organic resin additives on the process characteristics of the material. In addition, the microstructure of the material was studied with the electron microscope. The results of the optical-microscopic analysis are reported in Table 1. Photographs of sections of samples of base and modified compositions obtained with the electron microscope are shown in Fig. 4.

Important changes in the pore structure were observed in the sample containing the polyester resin. The total porosity decreased by 30% in comparison to the base composition, and the number of pores per unit of volume and in the plane of the section also decreased; the average pore size (average area, average perimeter) decreased, and the size of the walls between pores increased, while pores 0 – 0.2 mm in size totally disappeared.

The results of the electron-microscopic analysis confirmed the hypotheses concerning adsorption of the polymer films on the surface of the mineral components (especially silicic acid xerogel). Although the reaction of organic and inorganic polymers perhaps does not only consist of surface (adsorption) events alone. Since polymerization of the organic resin takes place parallelly with polycondensation and aggregation of molecules of $Si(OH)_4$ and these processes are superimposed in time, a more exhaustive chemical reaction; caused by partial copolymerization can take place.

It should be noted that the compositions based on liquid glass modified with organic resins are promising construction materials and are of great interest in the shortage of cement binder. The production technology for monosilicic construction materials is more ecological and less power-consuming than production of cement.

These materials can be used as an alternative to traditional concretes, since they have just as good basic process indexes (the strength characteristics are even higher than those for concretes in cement binder).

In addition, they can be used to manufacture articles for ornamental and architectural and construction applications that simulate natural stone, since they have such valuable properties as reproducing the shape impression and texture and color of articles and resistance to the external medium.

REFERENCES

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